Claims

1. A proton-conducting polymer membrane based on polyazoles which can be obtained by a process comprising the steps of

A) reacting one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or their esters which contain at least two acid groups per carboxylic acid monomer, or one or more aromatic and/or heteroaromatic diaminocarboxylic acids in the melt at temperatures of up to 350°C, preferably up to 300°C,

B) dissolving the solid prepolymer obtained in accordance with step A) in organic phosphonic anhydrides with formation of a solution and/or dispersion,

C) heating the solution obtainable in accordance with step B) under inert gas to temperatures of up to 300°C, preferably up to 280°C, with formation of the dissolved polyazole polymer,

D) forming a membrane using the solution of the polyazole polymer in accordance with step C) on a support and

E) treatment of the membrane formed in step D) until it is self-supporting.

2. The membrane according to claim 1, characterized in that, as aromatic tetraamino compounds, 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, 3,3',4,4'-tetraaminodiphenyl sulphone, 3,3',4,4'-tetraaminodiphenyl ether, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyldimethylmethane, are used.

3. The membrane according to claim 1, characterized in that, as aromatic dicarboxylic acids, isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid,1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenylsulphone-4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-

carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid or their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides are used.

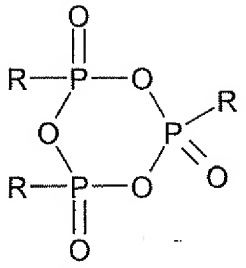
4. The membrane according to claim 1, characterized in that, as aromatic carboxylic acid, tricarboxylic acids, tetracarboxylic acids or their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides, preferably 1,3,5-benzenetricarboxylic acid (trimesic acid), 1,2,4-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid, 3,5,4'-biphenyltricarboxylic acid and/or 2,4,6-pyridinetricarboxylic acid, are used.

5. The membrane according to claim 1, characterized in that, as aromatic carboxylic acid, tetracarboxylic acids, their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides, preferably benzene-1,2,4,5-tetracarboxylic acids; naphthalene-1,4,5,8-tetracarboxylic acids; 3,5,3',5'-biphenyltetracarboxylic acid; benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, are used.

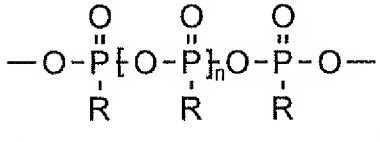
6. The membrane according to claim 4, characterized in that the content of tricarboxylic acid or tetracarboxylic acids (based on dicarboxylic acid used) is between 0 and 30 mol-%, preferably 0.1 and 20 mol-%, in particular 0.5 and 10 mol-%.

7. The membrane according to claim 1, characterized in that, as heteroaromatic carboxylic acids, heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids are used, which contain at least one nitrogen, oxygen, sulphur or phosphorus atom in the aromatic group, preferably pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid as well as their C1-C20 alkyl esters or C5-C12 aryl esters or their acid anhydrides or their acid chlorides.

8. The membrane according to claim 1, characterized in that, in step B), organic phosphonic anhydrides of the formula

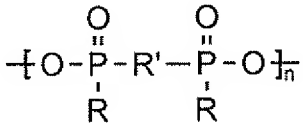


or linear compounds of the formula



$n \geq 0$

or anhydrides of the multiple organic phosphonic acids of the formula



$n \geq 1$

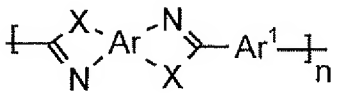
wherein the radicals R and R' are identical or different and represent a C_1-C_{20} carbon-containing group.

9. The membrane according to claim 1, characterized in that, in step B), a polyphosphoric acid having a content of at least 83%, calculated as P_2O_5 (by acidimetry), is additionally used.

10. The membrane according to claim 1 or claim 9, characterized in that, in step B), P_2O_5 is additionally used.

11. The membrane according to claim 1, characterized in that, in step B) or step C), a solution or a dispersion/suspension is produced.

12. The membrane according to claim 1, characterized in that, in step C), a polymer based on polyazole containing recurring azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII)



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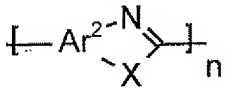
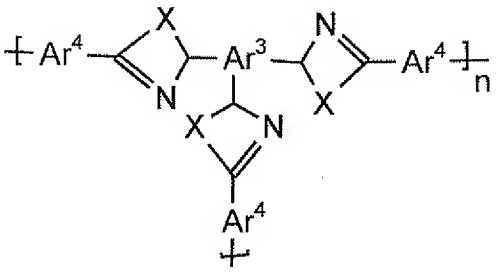


(II)



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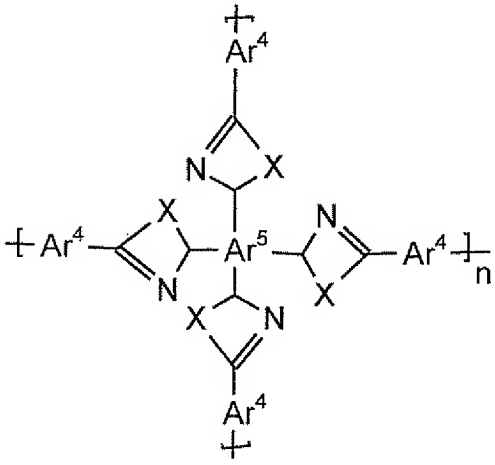
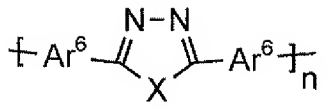
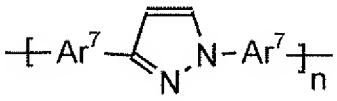


(IV)



(V)



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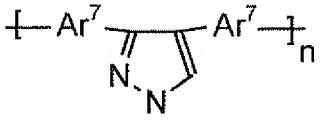

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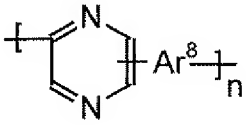

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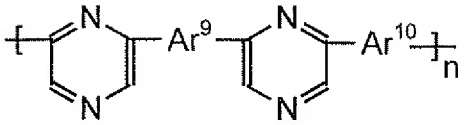

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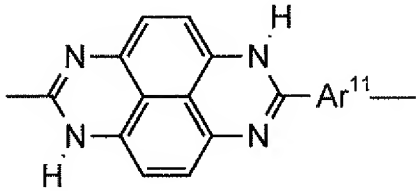
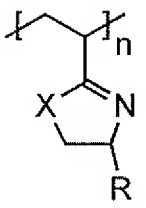


(X)



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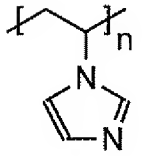

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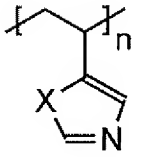

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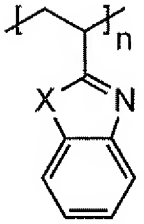
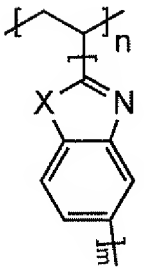


(XIV)



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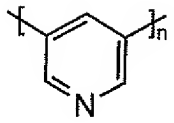
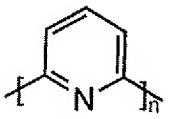
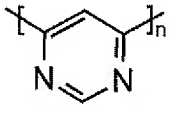


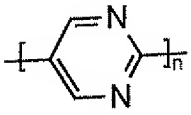
(XVI)



(XVII)



(XVIII)



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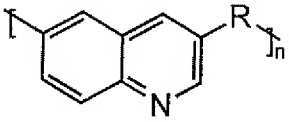
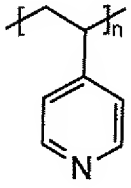
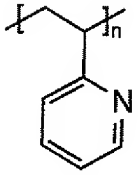


(XX)



(XXI)



(XXII)

wherein

Ar are identical or different and represent a tetracovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^1 are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^2 are identical or different and represent a bicovalent or tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^3 are identical or different and represent a tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^4 are identical or different and represent a tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^5 are identical or different and represent a tetracovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^6 are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^7 are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^8 are identical or different and represent a tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^9 are identical or different and represent a bicovalent or tricovalent or tetracovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^{10} are identical or different and represent a bicovalent or tricovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

Ar^{11} are identical or different and represent a bicovalent aromatic or heteroaromatic group which can be mononuclear or polynuclear,

X are identical or different and represent oxygen, sulphur or an amino group which carries a hydrogen atom, a group having 1 - 20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as a further radical,

R are identical or different and represent hydrogen, an alkyl group and an aromatic group, with the proviso that R in formula (XX) is not hydrogen, and

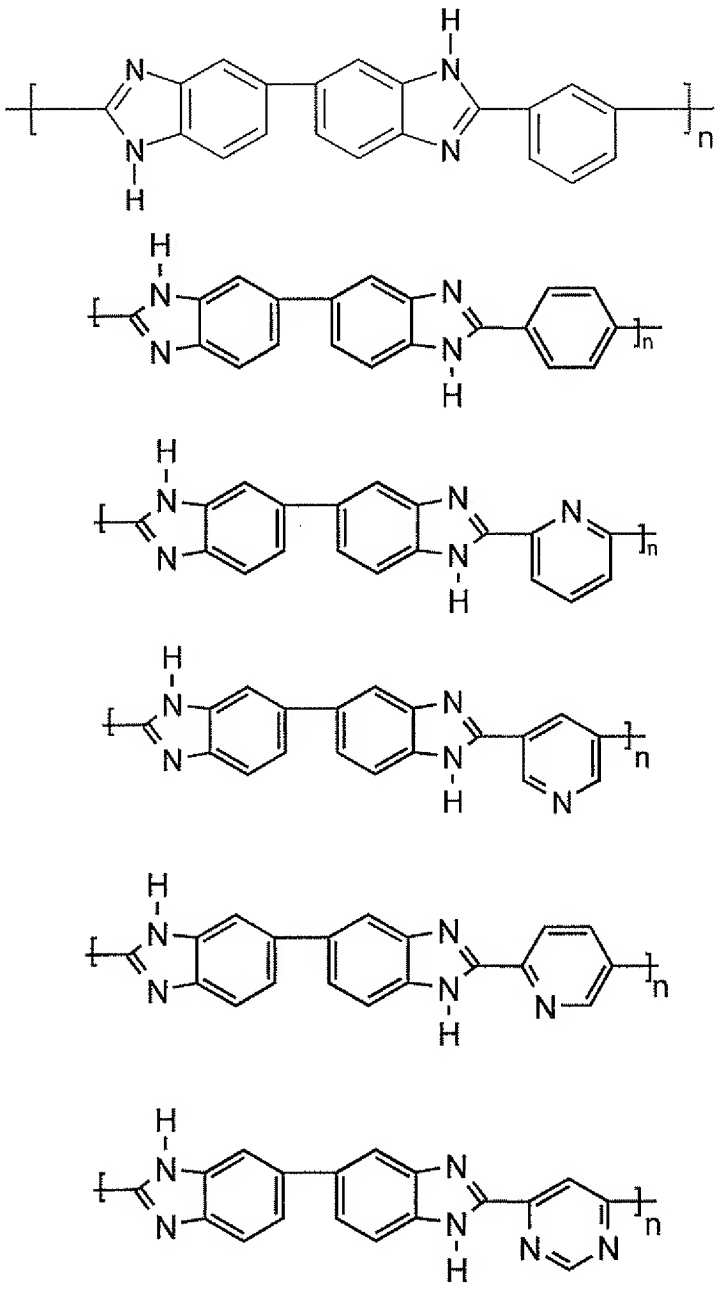
n, m are each an integer greater than or equal to 10, preferably greater than or equal to 100,

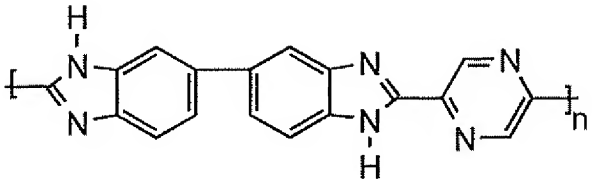
is formed.

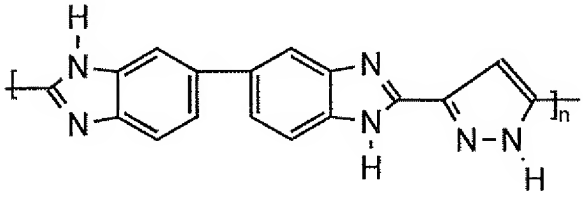
13. The membrane according to claim 1, characterized in that, in step C), a polymer selected from the group consisting of polybenzimidazole, poly(pyridines),

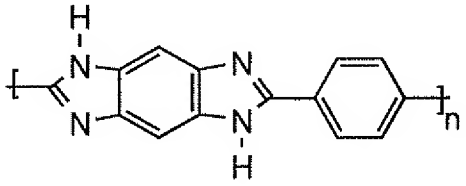
poly(pyrimidines), polyimidazoles, polybenzothiazoles, polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles and poly(tetrazapyrenes) is formed.

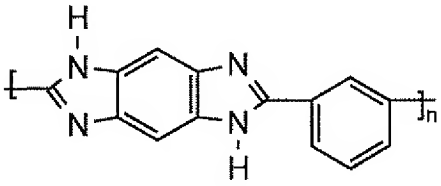
14. The membrane according to claim 1, characterized in that, in step C), a polymer containing recurring benzimidazole units of the formula

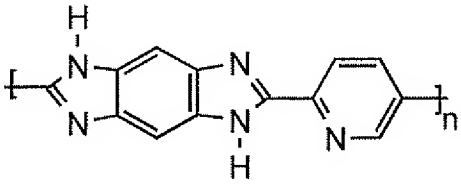












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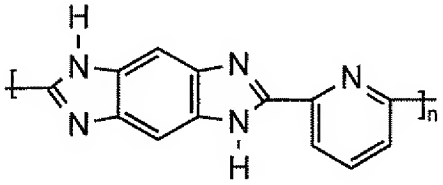

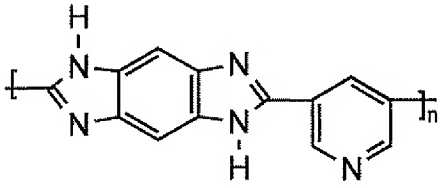

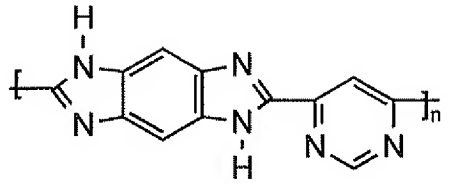

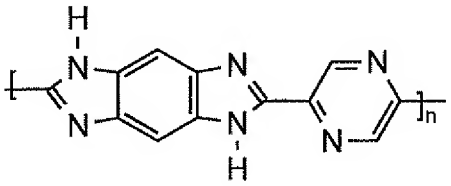

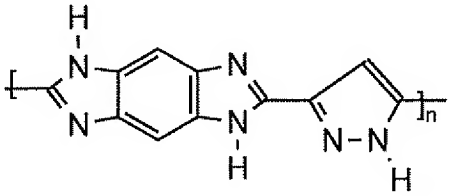

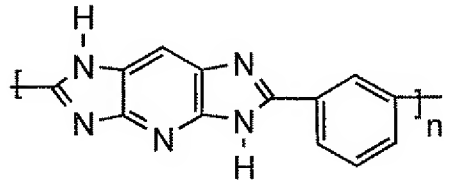

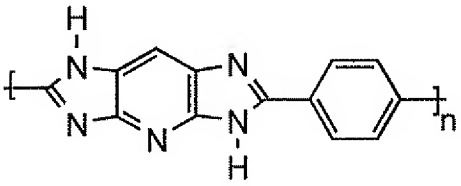

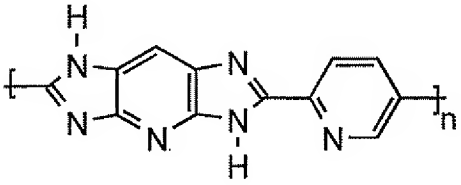

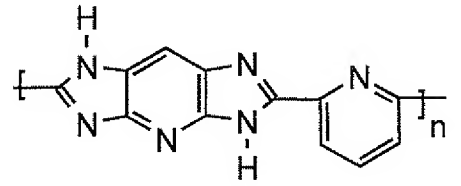

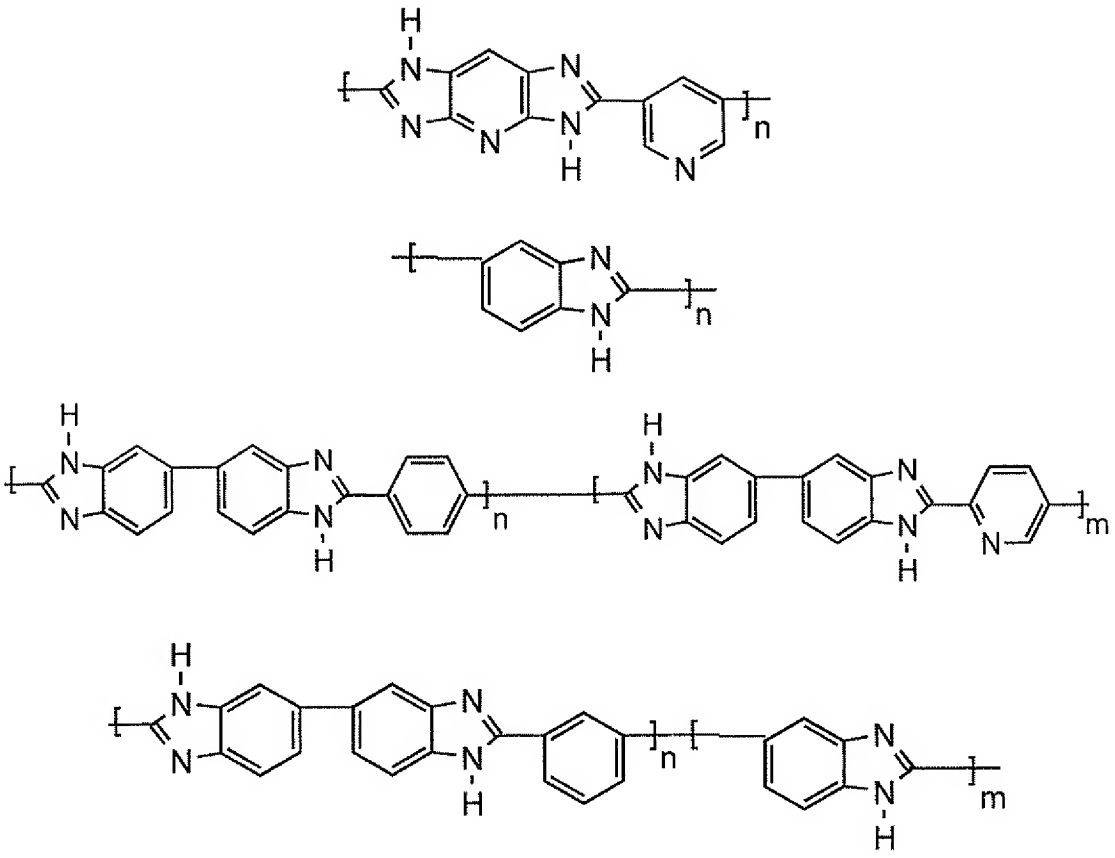

where n and m are each an integer greater than or equal to 10, preferably greater than or equal to 100, is formed.

15. The membrane according to claim 1, characterized in that, during or after step A), step B), step C), a further polymer is added as blend material.

16. The membrane according to claim 1, characterized in that, after step C) and before step D), the viscosity is adjusted by addition of phosphoric acid and/or organophosphonic acids.

17. The membrane according to claim 1, characterized in that the membrane produced in accordance with step E) is treated in the presence of moisture at temperatures and for a period of time until the membrane is self-supporting and can be detached from the support without any damage.

18. The membrane according to claim 1, characterized in that the treatment of the membrane in step E) is performed at temperatures of more than 0°C and less than 150°C, preferably at temperatures between 10°C and 120°C, in particular

between room temperature (20°C) and 90°C, in the presence of moisture or water and/or steam.

19. The membrane according to claim 1, characterized in that the treatment of the membrane in step E) is for 10 seconds to 300 hours, preferably 1 minute to 200 hours.

20. The membrane according to claim 1, characterized in that, in step D), an electrode is chosen as the support and the treatment in accordance with step E) is such that the membrane formed is no longer self-supporting.

21. The membrane according to claim 1, characterized in that, in step D), a layer having a thickness of 20 to 4000 µm, preferably between 30 and 3500 µm, in particular between 50 and 3000 µm, is produced.

22. The membrane according to claim 1, characterized in that the membrane formed in step E) has a thickness between 15 and 3000 µm, preferably between 20 and 2000 µm, in particular between 20 and 1500 µm.

23. An electrode having a proton-conducting polymer coating based on polyazoles which can be obtained by a process comprising the steps of

A) reacting one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or their esters which contain at least two acid groups per carboxylic acid monomer, or one or more aromatic and/or heteroaromatic diaminocarboxylic acids in the melt at temperatures of up to 350°C, preferably up to 300°C,

B) dissolving the solid prepolymer obtained in accordance with step A) in organic phosphonic anhydrides with formation of a solution and/or dispersion,

C) heating the solution obtainable in accordance with step B) under inert gas to temperatures of up to 300°C, preferably up to 280°C, with formation of the dissolved polyazole polymer,

D) forming a layer using the solution of the polyazole polymer in accordance with step C) on an electrode and

E) treatment of the layer formed in step D).

24. The electrode according to claim 23 where the coating has a thickness between 2 and 3000 µm, preferably between 3 and 2000 µm, in particular between 5 and 1500 µm.

25. A membrane electrode unit containing at least one electrode and at least one membrane according to one or more of claims 1 to 22.

26. The membrane electrode unit containing at least one electrode according to claim 23 or claim 24 and at least one membrane according to one or more of claims 1 to 22.

27. A fuel cell containing one or more membrane electrode units according to claim 25 or claim 26.